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HIGH RESOLUTION MASS SPECTRAL EXAMINATION OF THE RESIN  
FRACTION OF PETROLEUM ASPHALTICS

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INTRODUCTION

During the past years, several papers have been written which have discussed the properties of the asphaltic fraction of petroleum (5, 7, 10, 11). These studies were carried out on broad fractions and have resulted in a proposal for an average macrostructure of the molecule (4), which is consistent with a variety of data. The asphaltic structure has been pictured as a two-dimensional fabric of condensed aromatic rings, short aliphatic chains, and some naphthenic ring structure (12). The asphaltic molecules contain, in addition to carbon and hydrogen, varying amounts of nitrogen, oxygen, sulfur and metal (particularly vanadium and nickel). Most of the hetero elements are bound into ring structures since the molecules are extremely resistant to oxidation, and detectable functional groups appear to be absent (7). The individual sheets are held into unit cells by associative forces, and in concentrated solution these unit cells can associate further to form larger micelles (5). However, the structures of the individual sheets of the unit cell remain largely speculative and unexplained.

Mass spectral examination has been previously used to visualize the aromatic sheet portion of the asphaltic molecules (4). In these studies on the asphaltene fraction it was postulated that under 70eV impact voltage and at inlet temperatures exceeding 300°C, the aliphatic bonds might be broken, and the volatile fragment would be only the aromatic disk. If the bonds were not broken, and the structure were that of an aromatic sheet attached to a naphthenic net, the material might be expected to be so involatile as not to be seen by the mass spectrograph. In previous work the mass spectrum of the resin fraction (pentane soluble, propane insoluble) was observed to be very similar to that of the corresponding asphaltene (pentane-insoluble) fraction. This was taken as an additional indication of the similarity between the resin and asphaltene fractions. Since what was being seen in the mass spectrum was the aromatic portion of the resin molecule, which differed little from that of the corresponding asphaltene fraction, the difference between the resin and asphaltene molecules from the same crude oil would be only in the amount of the aromatic portion of the material. Also, it had been previously noted that the resin can be easily converted into asphaltenes by high temperature treatment (6), and at 300°C it would be expected that some conversion of the unsaturated naphthenic portion to the aromatic material might have occurred. This would, of course, make the resin fraction appear even more like an asphaltene. The present work is a continuation of the earlier studies (4), but with an improved inlet technique which permitted the resin fraction to be volatilized at lower temperatures and, thus, with less likelihood of being thermally altered. For this reason the mass spectra of these materials were of particular interest in providing information about the composition of the individual molecular sheets. The results of these exact mass measurements on the petroleum resin fractions represent the first attempt to describe exactly the unit sheet of the asphaltic molecule.

EXPERIMENTAL RESULTS

Mass spectra of a Boscan and a Baxterville resin were obtained using an AEI MS-9 spectrometer, equipped with a solid probe inlet system. Conditions for the measurement of this sample were: temperature, 250-270°C; impact voltage, 70eV. For high resolution measurements, slits were narrowed so as to give a resolution of one part in 15,000 (10% valley definition).

The inlet temperature is lower than that which was previously used. It was found possible to get material into the spectrometer at these lower temperatures and obtain a more reproducible

and a longer lasting pattern by depositing the resin onto crushed fire brick from benzene solution by allowing the benzene to evaporate, and packing the coated material onto the inlet probe. Of course, in order to get high resolution mass measurements, a stable, reproducible, relatively intense spectrum is required. At 70eV impact voltage, parent peaks as well as fragments from slightly higher mass ranges are to be expected.

The exact mass of selected peaks in this spectrum were measured by the peak-matching technique using perfluoro-*t*-butylamine as the standard. Approximately 60 peaks within each envelope were measured with an estimated accuracy of  $\pm 20$  ppm. Although the instrument is capable of mass measurements with an accuracy of 5 to 6 ppm, it was realized that such precision could not be achieved in view of the relatively low peak intensity. The error was estimated by remeasuring a given peak over a period of time and noting the variation in the measured value.

The possible molecular compositions for each peak were calculated using a computer program which required specification of the atom concentrations of carbon, hydrogen, nitrogen, oxygen and sulfur, and the mass range. The atomic concentration of the elements was selected to give a broad range of possibilities, probably much outside practical limits; e.g., this material has an average carbon composition of ca. 85%, which would indicate that at mass 400 there would be approximately 30 atoms of carbon per molecule. A range of carbon between 15 and 45 atoms per molecule was allowed for this calculation. In a similar fashion, the atom concentration of hydrogen was bracketed at 10 to 92, and nitrogen, oxygen and sulfur, between 0 and 5 atoms per molecule. It should be noted that, on the average, the concentration of sulfur in these materials is less than 6%, which would indicate less than 1 atom of sulfur per molecule (at mass 400); thus, at a limit of 5 atoms, it would seem that all reasonable possibilities would be covered. After the computer printed out the elemental composition possibilities, two additional tests were applied: 1. A calculation to determine whether each peak was parent or a singly-charged fragment by use of the formula  $(2) R = (2C - H + N + 2)/2$ . 2. A calculation of the hydrogen-to-carbon atom ratio. If *R* is a whole number, the peak is a parent; if it is fractional, the peak is a fragment. (Sulfur and oxygen do not effect the calculation since they are divalent.) Here *R* is defined as the total number of rings and/or double bonds which are present in a particular molecule. Since the resins have an average H/C atom ratio of 1.28, any formulations having values outside of the approximate range 1 to 1.6 were discarded as being unlikely. However, some pure hydrocarbon formulations were not discarded although they had low H/C values; also the limits were extended when the number of possibilities was small.

The possible formulas remaining after these operations are tabulated in Tables I and II along with the measured exact mass, the difference between this measured mass and the formula mass, the H/C atom ratio for the particular material, and the *R*-value. Table I lists parent peaks and fragment peaks of the Baxterville resin; Table II contains a similar tabulation for the Boscan resin.

Figure 1 shows a low (10eV) and high (70eV) impact voltage spectrum of the Boscan resin. All peaks were mass measured from the 70eV spectrum since the intensity of the low voltage spectrum did not allow exact mass measurement. The doubly-charged envelope can be seen at mass range 110 m/e to 220 m/e in the 70eV spectrum, showing that the fragment peaks which were measured at masses 250 m/e through 400 m/e are singly-charged species. Also, it should be noted that in the low voltage spectrum the most intense peaks appear, in general, at odd mass numbers.

## DISCUSSION

Work on the micro structure of the asphaltic materials involves the same two lines of attack that were used and are being used on the macro structure. These are to: 1. Carry out information gathering experiments, the results of which will be used to postulate possibilities for the structures. 2. Devise experiments which will confirm or deny these postulations. The exact mass measurement of some peaks in the resin fractions of the asphaltic material really fall into both categories.

Some average structures for asphaltic materials have been written (3,12) which utilize the results of NMR, elemental analyses, infrared measurements, etc. Therefore, an exact mass measurement can confirm the presence of postulated structures. In fact, the aromatic portion of the postulated structures could be rationalized as the type of formulation indicated by the mass spectra.

Equally important, however, is the exact mass measurement of given peaks which allows us to eliminate some possible structures and to determine that at a given molecular weight there is a limited number of structure possibilities. Many molecular compositions which were theoretically possible on the basis of molecular weight have been eliminated: 1. Because of their

variance from the allowed H/C atom ratio. 2. Because of the content of an excessive amount of hetero elements. In a material with an average of less than one atom of oxygen, nitrogen and sulfur per molecule, it would be unusual to find a portion which contained, in addition to four nitrogens, a variety of sulfur and oxygen groups. Therefore, the criterion used for elimination of peaks with excess hetero elements was that any peak containing more than six hetero elements was discarded. An exception was made for peaks which contained not more than three of one element, e.g.,  $\text{N}_3\text{O}_2\text{S}_2$  or  $\text{N}_2\text{O}_2\text{S}_3$  were saved, but  $\text{N}_3\text{O}_3\text{S}_2$  was discarded. If four of the hetero elements (e.g., three N and one S) were part of the metal ligand, it would seem likely that one or two hetero atoms could be found elsewhere in the molecule. Although none of these peaks can be unequivocally identified as porphyrin, such substances are seen in concentrated fractions (I). Table III lists all of the elemental combinations possible after consideration of only mass measurement and H/C ratio. The disposition of each possibility is indicated.

Several observations from the data are possible. Peaks which were chosen for measurement in the mass spectra were, of course, the ones that stood out most from the background. It is interesting that there is not a 14 mass difference in large peaks through the entire mass scale. This confirms the postulation that there are very few long paraffinic chains. If the breaking of a paraffinic chain were one of the features of the degradation of an asphaltic molecule, one would expect to find a series of peaks differing by the mass equivalent of a  $\text{CH}_2$  group as was found for pure alkyl substituted polynuclear aromatics or naphthenics. Peaks which differ by 32 mass units in a series are also not seen, which indicates that there is little loss of polymeric sulfur. In mass spectra run in these laboratories on asphaltic materials to which polymeric sulfur has been added, the spectra always show peaks differing by 32 mass units. These observations confirm previous postulations that hetero elements are, in general, bound in the ring structure.

Mass spectra run on model compounds both in these laboratories on alkyl polynuclear aromatics and work reported by Grubb and Meyerson (8) on alkyl substituted benzenes have shown that in substituted conjugated aromatic systems most fragment peaks are formed by either  $\alpha$  or  $\beta$  elimination with the latter predominant. In the case of methyl substituted aromatics, the predominant fragment peak is  $(\text{A}-\text{CH}_2)^+$ . The fragment peaks (Tables I and II) do, in fact, contain many structure possibilities which are only one mass unit removed from a peak in the parent listing. As substitution increases ( $\text{A}-\text{CH}_2-\text{R}$ ,  $-\text{R}'$ ,  $-\text{R}''$ ) a combination of  $\alpha$  and  $\beta$  cleavage results in the same predominant fragment  $(\text{A}-\text{CH}_2)^+$ . Fragments formed in this fashion should have little aliphatic substitution and, therefore, a high R-value. Perhaps, several more of the peaks might have been eliminated (e.g., mass number 269.1335 in Table I, the  $\text{C}_{14}\text{H}_{21}\text{O}_5$  compound containing only four rings per molecule is much more unlikely than either of the other two possibilities). Further, at mass number 277.1938 both of the first two possibilities might be eliminated leaving the hydrocarbon as the most likely constituents. Also, it is probable that the fragments are largely devoid of side chains, and it is observed that the hetero element distribution varies little between the parent and fragment peaks (Tables IV and V). These are further indications that the hetero elements are most probably in the rings. Tables IV and V ignore the atom concentrations of C and H, which vary greatly, and consolidate the different combinations of hetero elements in the resins for ease of comparison of parent with fragment composition.

The similarity between the R-values and the hetero element composition for the parent and fragment peaks could well be an indication of the polymeric nature of these materials. The parents would be unpolymerized monomers similar to the components of the polymerized higher molecular weights species.

As previously noted, the low voltage spectrum in the range of peaks that were mass measured shows the most intense peaks to have odd mass numbers, indicating an odd number of nitrogens present. The presence of an odd number of nitrogens was not used as a criterion for eliminating parent peaks in the tables; however, it is consistent with the independent observation from EPR examination that some of the ligands to vanadium present in the asphaltic materials may be composed of three nitrogens and another hetero element (probably oxygen or sulfur) rather than four nitrogens as found in the case of porphyrin (9).

If a more accurate mass measurement could be made, many more of these peaks could be eliminated; therefore, this work is at a very preliminary stage, and a study of introduction techniques which will introduce more material into the instrument and allow more accurate measurements is being undertaken.

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